Supporting Online Material

Methods and Materials

CsH_2PO_4 preparation. Cesium dihydrogen phosphate powder was synthesized by methanol-induced precipitation from aqueous solutions of stoichiometric quantities $CsCO_3$ and H_3PO_4. The resulting precipitate was dried under vacuum at 100 °C.

Thermal analysis. Simultaneous gravimetric analysis and differential scanning calorimetry was performed using a Netzsch Jupiter 449c, equipped with a Balzers AMU 200 mass spectrometer for exhaust gas analysis. Data were collected from 30 to 400 °C at a heating rate of 5 °C min^{-1}. Samples were heated under 60 cm^3 min^{-1} flowing gas, with gas compositions of 4 vol % H_2 in Ar and 15 vol % O_2 in Ar for the first and second experiment, respectively.

Dehydration experiment. Equilibrium dehydration pressures were measured by placing a small quantity of CsH_2PO_4 and various amounts of H_2O in an enclosed, heated chamber equipped with a humidity sensor. The pressure in the chamber was recorded as a function of temperature and the onset of dehydration marked by a rapid increase in p_{H_2O}.

MEA fabrication. Single-cell fuel cells, or MEAs were fabricated using carbon Toray paper as electrodes and a mixture of Pt, CsH_2PO_4, carbon, naphthalene in a 10:6:1:1 weight ratio in the electrocatalyst layer (18 mg Pt cm^{-2}). In the case of the direct methanol fuel cell, the anode electrocatalyst layer was replaced with a mixture of $Pt_{0.5}Ru_{0.5}$ alloy, CsH_2PO_4, C, naphthalene in an 8:6:1:2 weight ratio (13 mg PtRu cm^{-2}). The multi-layer structure was cold-pressed under uniaxial pressure at 340 MPa. Upon

heating to the temperature of fuel cell operation, naphthalene sublimed, ideally leaving behind a porous electrode structure. Electrochemical characterization was carried out on three different H_2/O_2 cells and one DMFC cell.

Electrochemical measurements. The sample was placed in an in-house constructed fuel cell measurement station and polarization curves collected using a Keithley 2420 Source Meter. In the case of the H_2/O_2 cell, humidification was maintained by passing oxygen and hydrogen through water held at 69-72 °C , in order to obtain the desired water partial pressure of 0.3 atm. For the direct methanol fuel cell, argon was passed through hot water (70 °C), and gaseous methanol was added to the humidified argon stream. The $CH_3OH:H_2O$ molar ratio was held at 0.92. The water partial pressure at the cathode was maintained at 0.33 atm.. Humidity levels were monitored with an accuracy of 1 % using an EdgeTech 650 capacitance-based sensor.

Supporting Text

Consequence of water partial pressure on fuel cell operation

In order to confirm the necessity for controlling water partial pressure when operating CsH_2PO_4 electrolyte fuel cells at elevated temperatures, a CsH_2PO_4-based membrane electrode assembly was fabricated and measured in an H_2/O_2 fuel cell configuration. The cell was operated at 242 °C under humidified 50 sccm flowing gasses, $p_{H_2O} = 0.3$ atm. The water partial pressure was decreased stepwise, measuring polarizations curves (current density versus cell voltage) at each step. Below $p_{H_2O} = 0.105$ atm, the cell became non-operational. From Fig. 1 in the main text, the onset of dehydration at 242 °C is not expected until $p_{H_2O} = 0.06$ atm, however, factoring a ± 3 °C error in the measured

temperature, these values are reconcilable. These results show that it is essential to maintain the appropriate water partial pressure to suppress the dehydration of CsH_2PO_4 when operating a CsH_2PO_4 electrolyte fuel cell at elevated temperatures.

Supporting Figures

H_2/O_2 fuel cell stability measurement for 35 hours

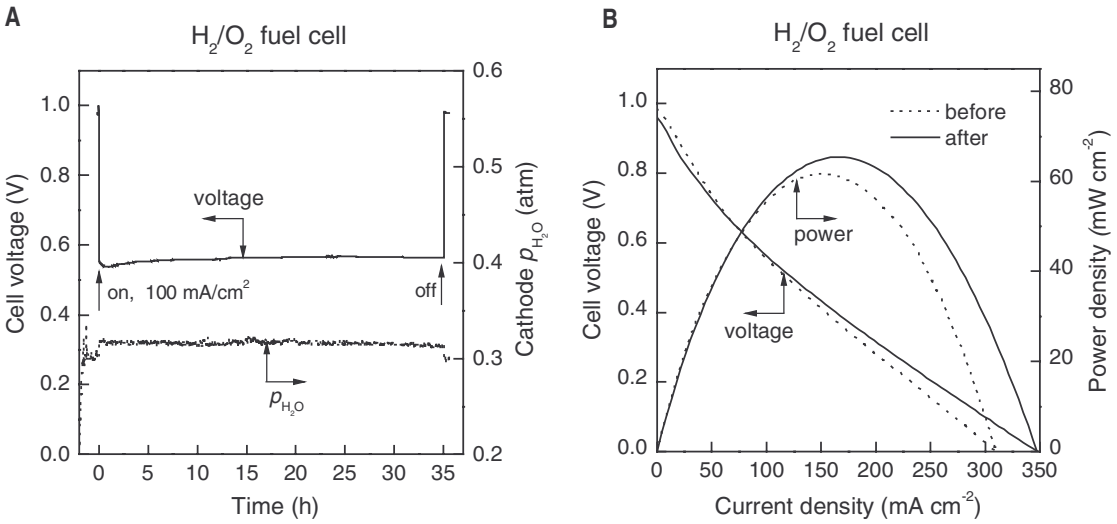

Fig. S1. H_2/O_2 fuel cell performance with CsH_2PO_4-based electrolyte. (**A**) Cell voltage and water partial pressure as a function of time while drawing 100 mA cm^{-2} continuous current for 35 h. (**B**) Cell voltage and power density versus current density before and after 35 h measurement. The cell was operated at 235 °C under humidified (p_{H_2O} = 0.3 atm) 50 sccm flowing H_2 and O_2 gases at the anode and the cathode, respectively. Electrolyte thickness was 260 µm and catalyst loading 18 mg cm^{-2} Pt. During the continuous measurement, the voltage very gradually increased from 0.538 to 0.567 V, with an average of 0.561 V. Water generated at the cathode was in correspondence with that expected from drawing 100 mA cm^{-2} current (Fig. S2). The polarization curves obtained before and after the long-term evaluation were similar to one another, although not identical. The open cell voltage (OCV) was initially 0.986 and dropped to 0.960 V after 35 hr measurement. An initial drop in OCV has been observed in similar cells and is attributed to evolution of the electrocatalyst layer.

Water generated at the cathode for H_2/O_2 fuel cell

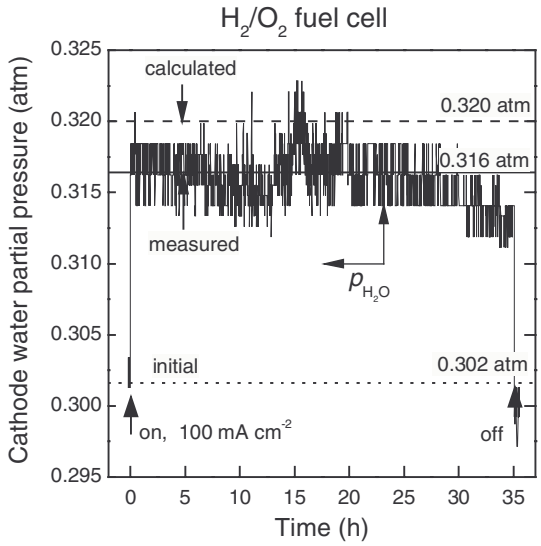

Fig S2. Cathode water partial pressure as a function of time for a CsH_2PO_4 electrolyte H_2/O_2 fuel cell while 100 mA cm^{-2} of current was drawn continuously for 35 h. The cell was operated at 235°C. Flowing 50 sccm humidified, p_{H_2O} of 0.302 atm (*initial*—dotted line), H_2 and O_2 gases were fed to the anode and cathode, respectively. While drawing current the average p_{H_2O} was 0.316 atm (*measured*—solid line). The water partial pressure was measured with an accuracy of ± 1 %. The water generated at the cathode corresponding to 100 mA cm^{-2} current is 7.06 x 10^{-5} mol min^{-1} H_2O, p_{H_2O} of 0.320 atm (*calculated*—dashed line), which is within experimental error of 5(3) x 10^{-5} mol min^{-1} H_2O measured from the change in water partial pressure.

Ohmic loss due to electrolyte resistance

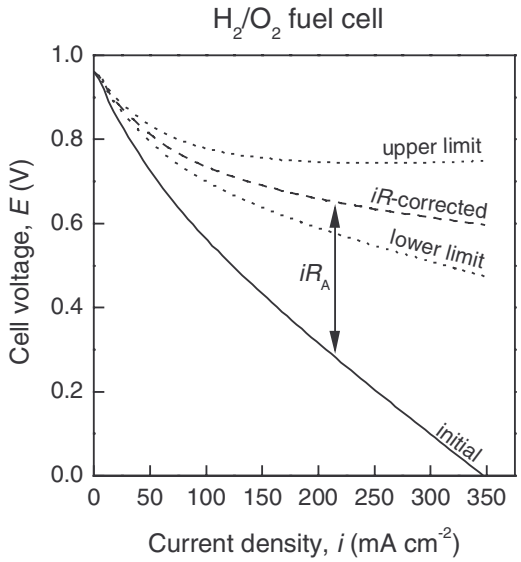

Fig. S3. The current density versus cell voltage for a CsH_2PO_4-based H_2/O_2 fuel cell operated at 235°C, p_{H_2O} = 0.3 atm. The cell was composed of a 260 μm thick CsH_2PO_4 electrolyte. The *iR-corrected* result (dashed line), and *upper* and *lower limit* (dotted lines) are calculated from the *initial* (solid line) measured cell voltage E, current density i, and area specific resistance of the electrolyte R_A, $iR\text{-}corrected = E - iR_A$. The area specific resistance of the electrolyte R_A is calculated from the electrolyte thickness t and conductivity σ, $R_A = t/\sigma$. Values of conductivity were obtained from the Arrhenius relationship: $\sigma(T) = A/T \exp(-\Delta H_a / k_B T)$, where the pre-exponential factor A and activation enthalpy ΔH_a obtained from Baranov *et al.* (*1*) are 2.7 x 10^{-3} Ω^{-1} cm^{-1} K and 0.29(1) eV, respectively. Using these values, the conductivity of CsH_2PO_4 is 1.5×10^{-2} Ω^{-1} cm^{-1} at 235°C, with an upper and lower limit of 1.9×10^{-2} and 1.2×10^{-2} Ω^{-1} cm^{-1}, respectively. As seen from above, the accuracy of the *iR-corrected* result is heavily dependent upon accurate values of conductivity. Nonetheless, the majority of voltage losses can be attributed to the resistance of the electrolyte.

Onset of dehydration in CsH_2PO_4

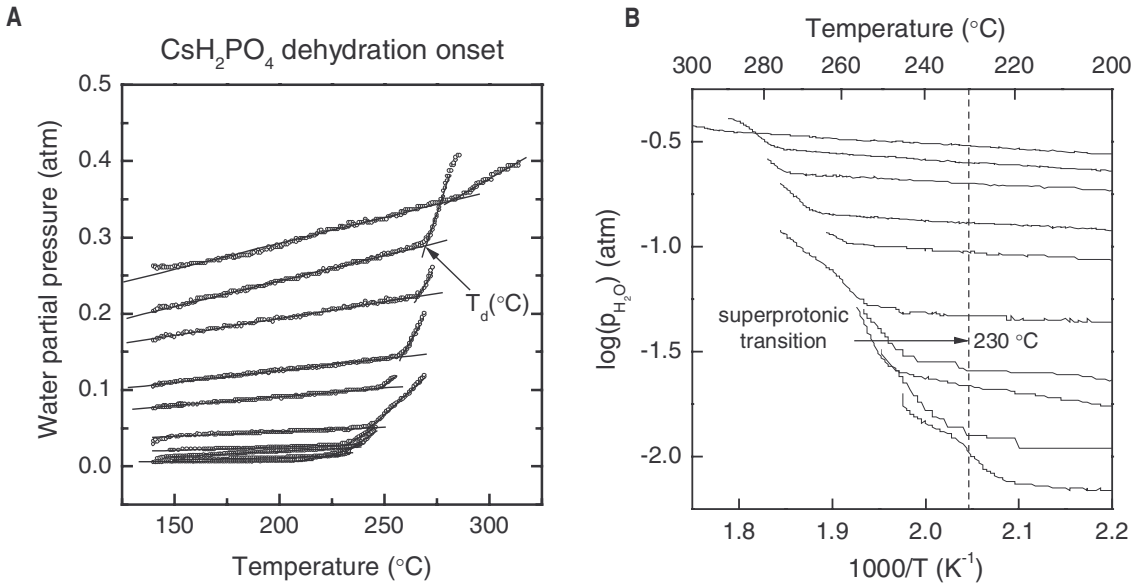

Fig. S4. (**A**) Water partial pressure (p_{H_2O}) as a function of temperature for CsH_2PO_4 powder at various initial starting water partial pressures. (**B**) Arrhenius plot of p_{H_2O} as a function of temperature. Powder samples of CsH_2PO_4 at ten different starting water partial pressures were heated at 0.4 °C min^{-1} to ~ 300 °C in a closed volume container. Accuracy of recorded temperature was ± 3 °C. Onset of dehydration (T_d), indicated by a discontinuous change in the slope of p_{H_2O} as a function of temperature, is shown in (**A**). In (**B**), no clear Arrhenius behaviour was observed that would indicate a single dehydration reaction and corresponding Gibbs free energy (ΔG_r) for the dehydration CsH_2PO_4. Though a clear change in slope is expected at 230 °C resulting from the change in entropy through the superprotonic phase transition, unexpected, and indicative of the formation of an intermediate compound, was the observation of a liquid phase at ~ 290 °C, a temperature well below the melting point of CsH_2PO_4 or $CsPO_3$. It is likely that the dehydration of CsH_2PO_4 takes place via a series of polymorphic intermediates which melt at relatively low temperatures. This conclusion is, in part, substantiated both by the absence of Arrhenius behaviour upon heating and a of a reverse reaction upon cooling.

Supporting Tables

Table I. Summary of performance characteristics of three additional CsH_2PO_4-based H_2/O_2 fuel cells. Each cell was prepared in the same fashion, with a CsH_2PO_4 electrolyte thickness of 260 µm, catalyst loading of 18 mg cm^{-2} Pt, and humidified gasses (p_{H_2O} = 0.3 atm).

Cell No.	Open Circuit Voltage (V)	Short Circuit Current Density (mA cm^{-2})	Peak Power Density (mW cm^{-2})
1	0.960 – 0.986	308 – 348	61.7 – 65.4
2	1.003 – 1.027	308 – 383	49.3 – 60.3
3	0.915 – 0.948	323 – 361	50.5 – 58.1

Supporting References and Notes

1. A.I. Baranov, V.P. Khiznichenko, V. A. Sandler, L. A. Shuvalov, *Ferroelectrics* **81**, 183 (1988).